

Absorption and Luminescence in $\text{PbX}_2\text{-SnX}_2$ (X=Cl, Br) Mixed Crystals

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Absorption and luminescence properties have been investigated extensively at low temperatures in $\text{PbX}_2\text{-SnX}_2$ (X = Cl, Br) in order to get the structural information on the self-trapped excitons, electrons and holes in crystals of the PbCl_2 structure. The crystal structure of lead and tin halides (chloride and bromide) is orthorhombic D_{2h}^{16} [1]. The coordination number is 9 for Pb^{2+} (Sn^{2+}) and 4 (site-4) or 5 (site-5) for Cl^- (Br^-). In lead and tin halides, the top of the valence band is composed of $6s$ ($5s$) orbits of Pb^{2+} (Sn^{2+}) with considerable mixing from np orbits of halogen ions and the bottom of the conduction band is mainly composed of $6p$ ($5p$) orbits of Pb^{2+} (Sn^{2+}) [2, 3].

Lead halide crystals have been well known as typical materials showing photolysis with ultraviolet light or X-ray irradiation at room temperature [4]. In PbCl_2 and PbBr_2 crystals, two kinds of intrinsic luminescence are observed under ultraviolet excitation at low temperature [2, 3]. The one is observed at 3.78 eV (UV) in PbCl_2 and at 2.75 eV (B) in PbBr_2 which is excited only in the lowest energy excitonic absorption band and is connected to the self-trapped excitons (STE) [5]. The other appears at 2.62 eV (BG) in both crystals only under excitation in the band-to-band transition region and is attributed to the recombination of self-trapped electrons (STEL) with holes [6]. Electrons are self-trapped to result in $(\text{Pb}_2)^{3+}$ -diatomic molecular centers as verified from the EPR studies [7].

In the present work, absorption and luminescence due to Sn^{2+} ions doped in PbCl_2 and PbBr_2 have been investigated at low temperatures in order to explicate the role of cations in the lattice relaxation processes of photo-excited states. The dopant Sn^{2+} ion has the same outer electronic configuration $(5s)^2$ as the host Pb^{2+} ion $(6s)^2$.

By doping a small amount of Sn^{2+} ions in PbCl_2 , two absorption band structures are observed at 3.65 and 3.86 eV well separated from the lowest excitonic absorption band of the host PbCl_2 lattice at 4.68 eV [2]. They are attributed to the intra ionic transitions of the dopant Sn^{2+} ions from the $^1\text{S}_0$ state of the $(5s)^2$ ground configuration to the $^3\text{P}_1$ state of the $(5s)(5p)$ excited configuration. The separation energy of 1.03 eV between the lowest energy absorption bands due to the dopant tin ions and the lowest energy excitonic absorption band corresponds to the difference in ionic excitation energy (1.14 eV [8]) from the $^1\text{S}_0$ to the $^3\text{P}_1$ state of the Sn^{2+} and the Pb^{2+} ions. The $^3\text{P}_1$ state further splits into three irreducible states, Γ_1 and $2\Gamma_2$ states, by the C_s crystal field at the Pb^{2+} ion site in PbCl_2 , which would be responsible for the observed absorption structures. The dichroic absorption measurement is expected to give more reliable assignment for these absorption structures.

Two new emission bands (R_1 -emission at 1.90 eV and R_2 -emission at 1.65 eV) due to the doped Sn^{2+} -ions were found at low temperatures with excitation in the absorption region specific to the doped tin ions just described above. The R_1 -emission is excited strongly in the 3.65 eV absorption band while the R_2 -emission in the 3.86 eV absorption band and higher energy region. The R_1 -emission shows similar behavior to the intrinsic UV-emission in their excitation spectra and is connected to the $[\text{Sn}^+(\text{Cl})_3 + \text{hole}]$ center on the analogy of the $[\text{Pb}^+(\text{Cl})_3 + \text{hole}]$ center for the intrinsic UV-emission of PbCl_2 [5]. This type of luminescence centers are realized by making covalent bonds between central tin or lead ions and three 5-site halogen ions through sp^2 hybridization in the course of lattice

relaxation of the photo-excited state. The origin of the R_2 -emission is not clear at present although it might be supposed to come from the $[(\text{PbSn})^{3+}\text{-STEL} + \text{hole}]$ center because of its excitation region extending higher energy region. This type of diatomic self-trapped electron centers have been confirmed in PbCl_2 as $(\text{Pb}_2)^{3+}\text{-STEL}$ centers [7] and in $\text{PbCl}_2\text{:Tl}^+$ as $(\text{PbTl})^{2+}$ centers [9] which are responsible for the recombination emissions, namely the BG-emission in PbCl_2 [6] and a green emission in $\text{PbCl}_2\text{:Tl}^+$ [10]. In case of excitation in the excitonic and the band-to-band absorption region of the host PbCl_2 , the intrinsic UV- and BG-emission are observed, respectively.

In conclusion, the doped tin ions produce well-defined absorption structures that are attributed to intra ionic transitions of the tin ions. Two emission bands specific to the doped tin ions are observed with excitation in the tin absorption bands, which are related to the intrinsic STE and recombination luminescence. The results on the dichroic properties, temperature dependence, luminescence decay behaviors will be presented together with those obtained in the $\text{PbBr}_2\text{-SnBr}_2$ system.

References

- [1] A.F.Wells: *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1977) p. 221.
- [2] M. Fujita, M. Itoh, Y. Bokumoto, H. Nakagawa, D.I. Alov, M. Kitaura: *Phys. Rev. B* **61** (2000) 15731.
- [3] A.S. Voloshinovskii: *Sov. Phys. Solid State* **35** (1993) 1588.
- [4] J.F. Verway: *J.Phys.Chem.Solids* **31** (1970) 163-171.
- [5] M. Kitaura, H. Nakagawa: *J. Luminescence* **72-74** (1977) 883.
- [6] M. Kitaura, H. Nakagawa: *J.Electron Spectroscopy and Related Phenomena* **79** (1996) 171.
- [7] S.V. Nistor, E. Goovaerts, D. Schoemaker: *Phys. Rev.B* **48** (1993) 9575
- [8] C.E. Moore: *Atomic Energy Levels* Vol. III (Circular of the National Bureau of Standards 467, USA, 1958) p.82 & p.213.
- [9] S.V. Nistor, E. Goovaerts, D. Schoemaker: *Phys. Rev. B* **57** (1998) 1.
- [10] H.Nakagawa, M.Terakami, K.Yasuda: Book of Abstracts of 4th Euro-Conference on Luminescent Detectors and Transformers of Ionizing Radiation, OWE-5, 35 (2000,8), to be published in Radiation Measurements.